

Factors affecting the “non-cleanables” measurement of resist outgas testing: interpreting the null results

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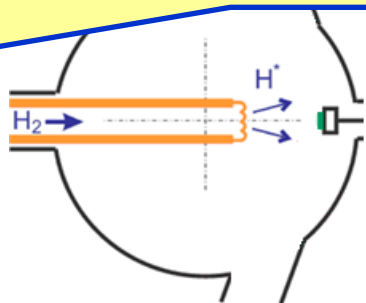
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ASML Resist-Outgas Testing Protocol at NIST

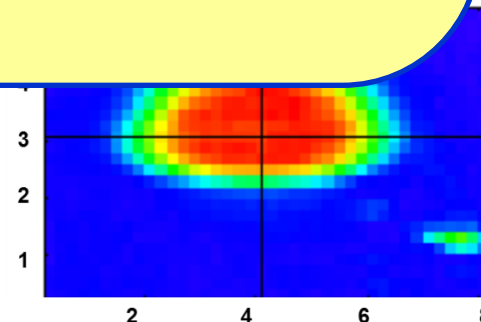
- Referred to as “non-cleanables,” yet no resist has ever failed due to non-C residuals.
- Typically XPS does not detect atomic concentrations significantly above background levels of S.
- F is rarely observed (in contamination spot) despite being common resist component.
- Resist developers may avoid elements like iodine with high PAG quantum efficiency due to potential contamination risk.
- Systematic study of actual contamination threat posed by non-C outgas species is needed.

(5)
Measure amount
of residual non-C
{S, P, F, I, Cl, ...}
with XPS.



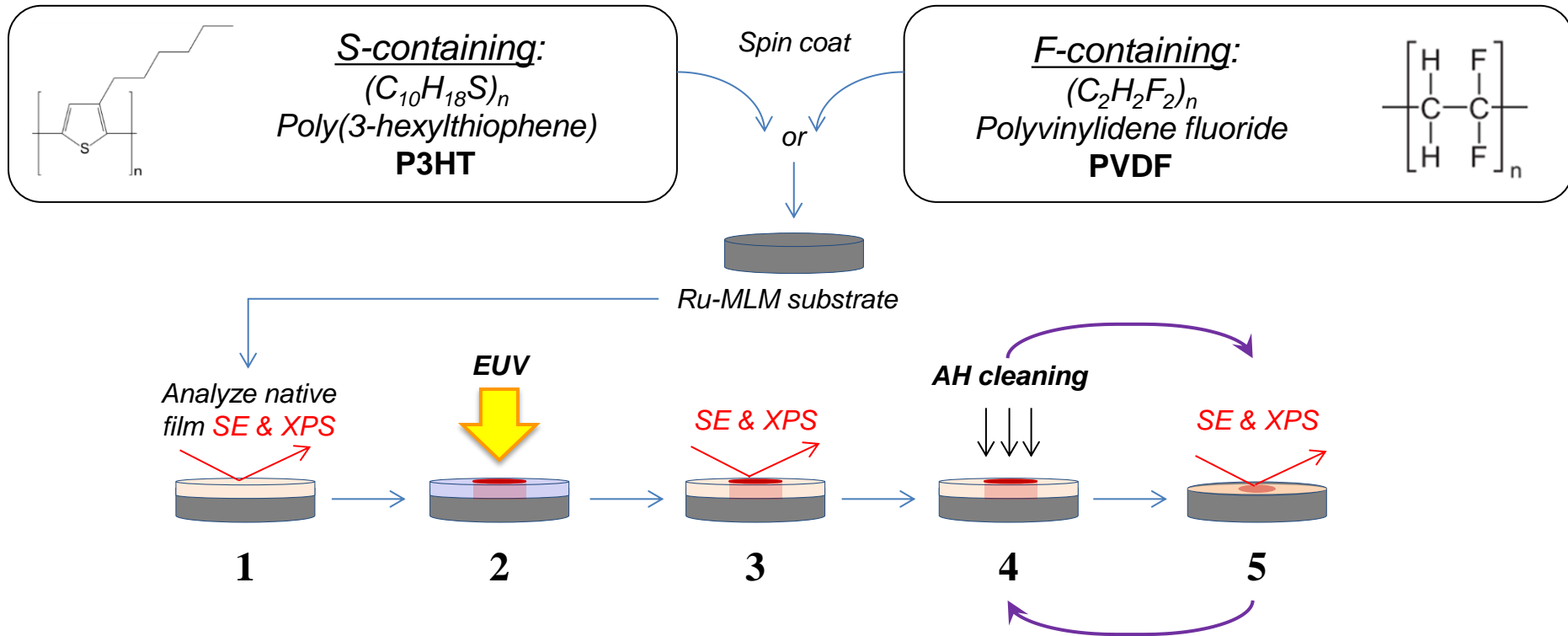
(4) Clean C with atomic H

<3nm



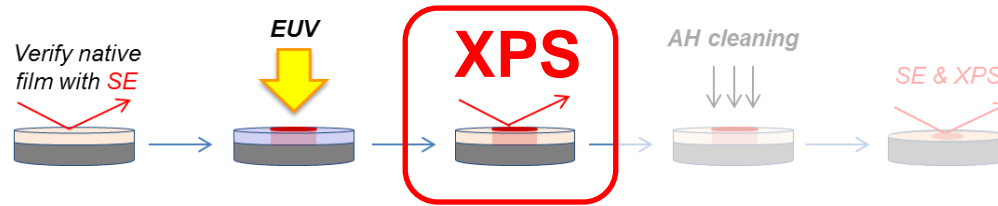
(3) Measure C-thickness with
spectroscopic ellipsometry
and scale to 300 mm wafer

EUV/e-beam exposure of polymer films

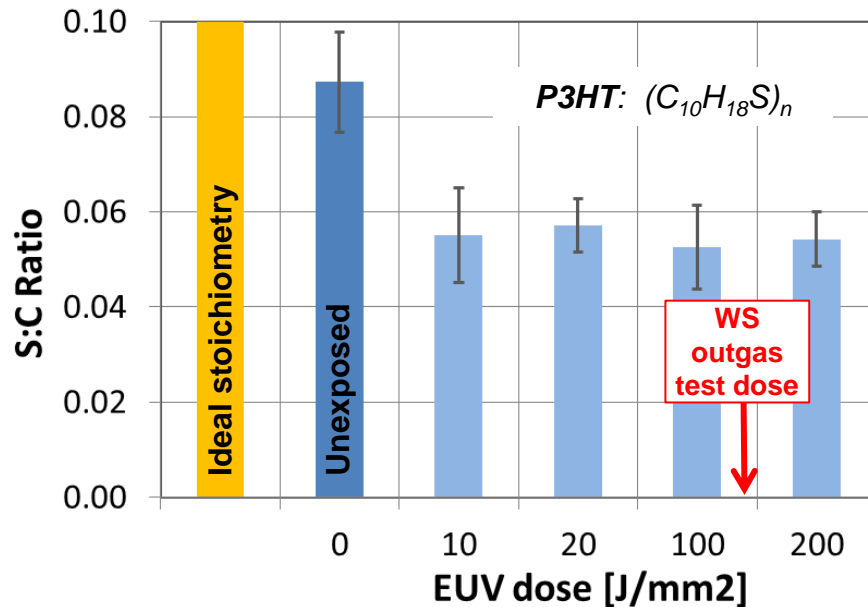


- 1) Spin coat <10 nm film of polymer onto Ru-cap MLM substrate & characterize
 - 2) Perform EUV/e-beam exposures with varying dose
 - 3) Characterize changes with spectroscopic ellipsometry (SE) and XPS
 - 4) Subject to atomic-H (AH)
 - 5) Characterize with SE and XPS
- } Repeat to determine cleaning rate

EUV interaction with P3HT and PVDF

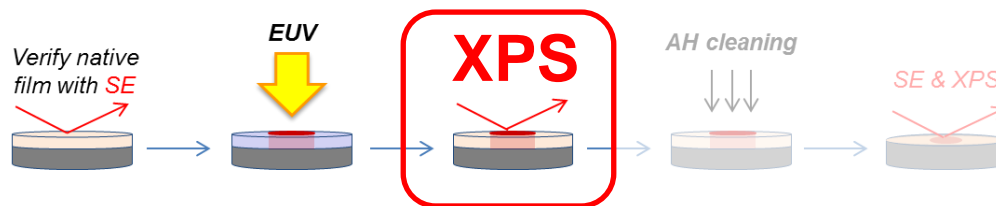


S is partially desorbed by EUV

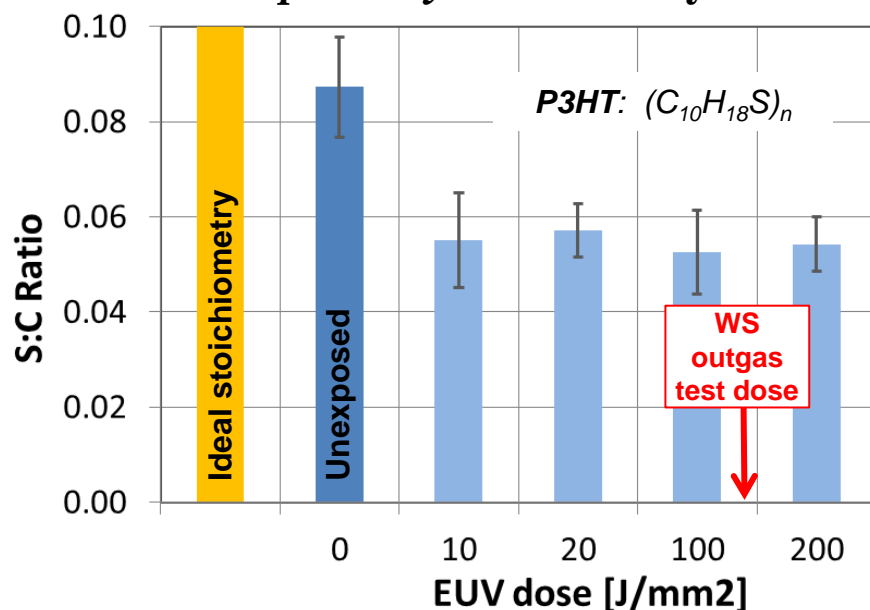


- ~ 40% of S is rapidly desorbed by EUV (<10 J/mm²)
- ~60% of S is resistant to desorption by highest doses
- No evidence of C desorption

EUV interaction with P3HT and PVDF

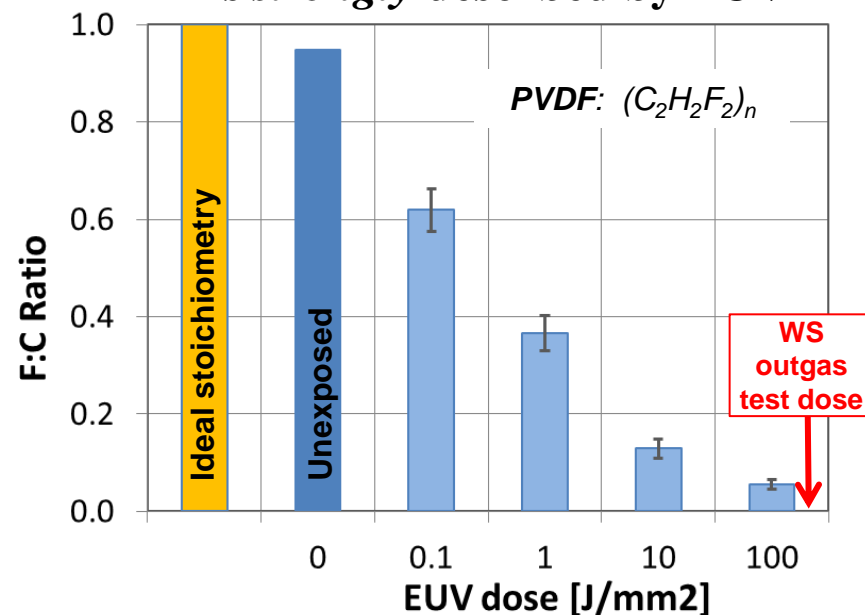


S is *partially* desorbed by EUV



- ~ 40% of S is rapidly desorbed by EUV (<10 J/mm²)
- ~60% of S is resistant to desorption by highest doses
- No evidence of C desorption

F is *strongly* desorbed by EUV

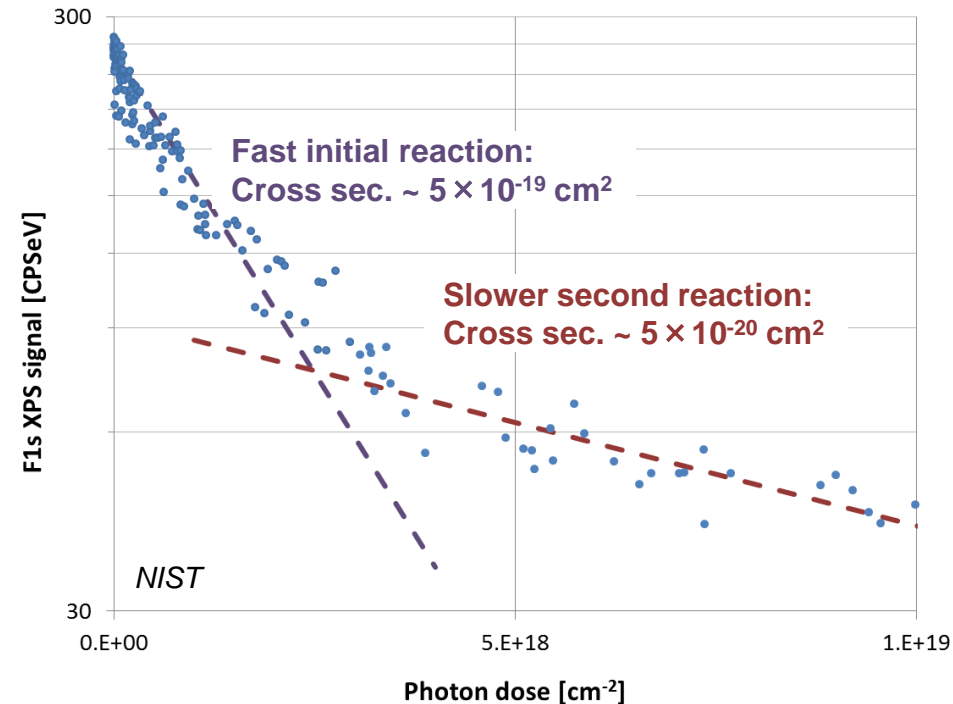


- ~50% of F is rapidly desorbed by low doses
- F continues to desorb with increasing dose
- No evidence of C desorption

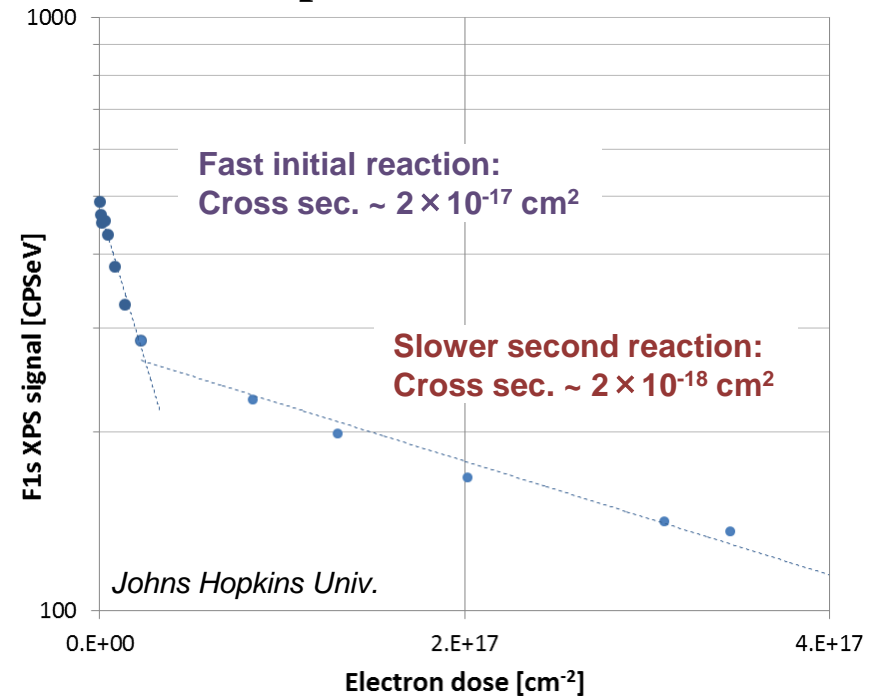
- Consistent with x-ray-induced desorption of F but not S during XPS measurements (observed by EIDEC and confirmed in collaboration with NIST)

Compare EUV & e-beam desorption of F from PVDF

PVDF exposed to **EUV**

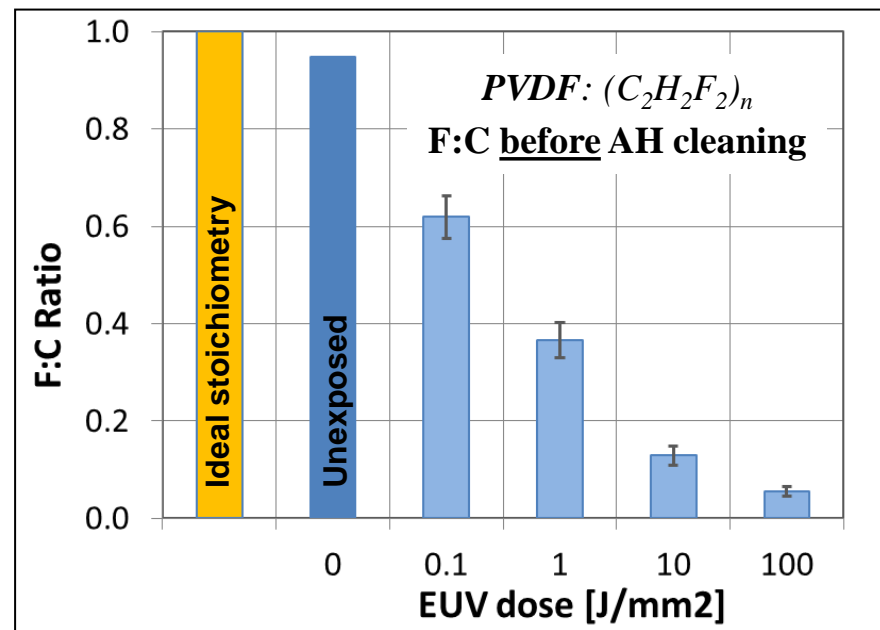
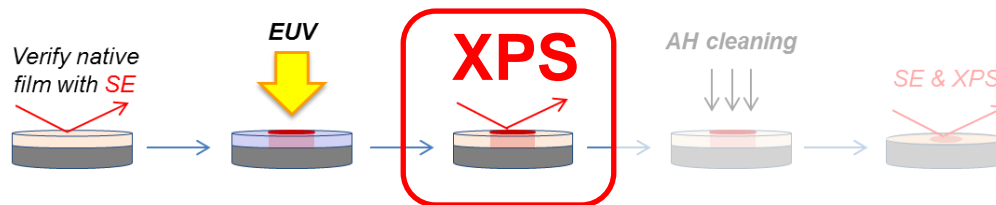


PVDF exposed to 2keV **e-beam**

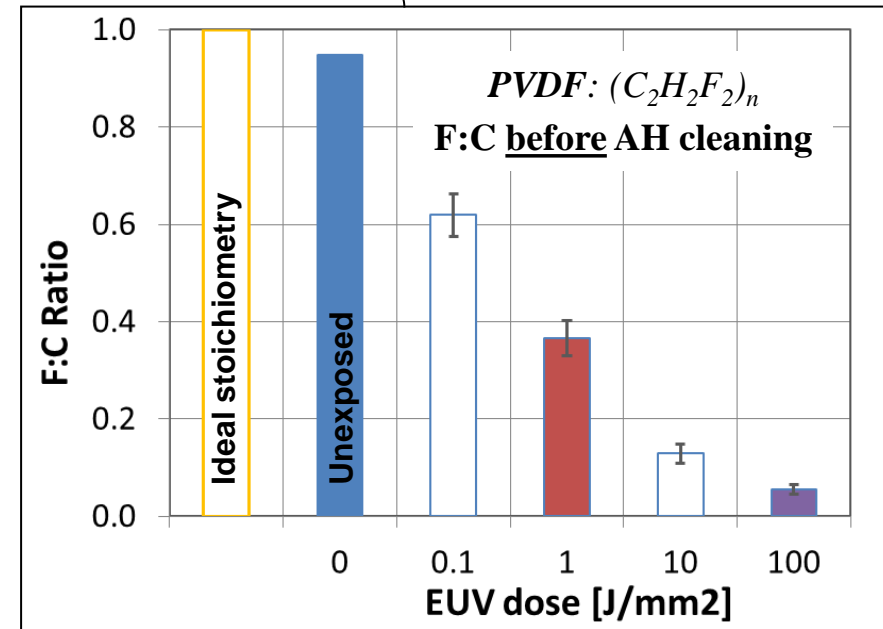
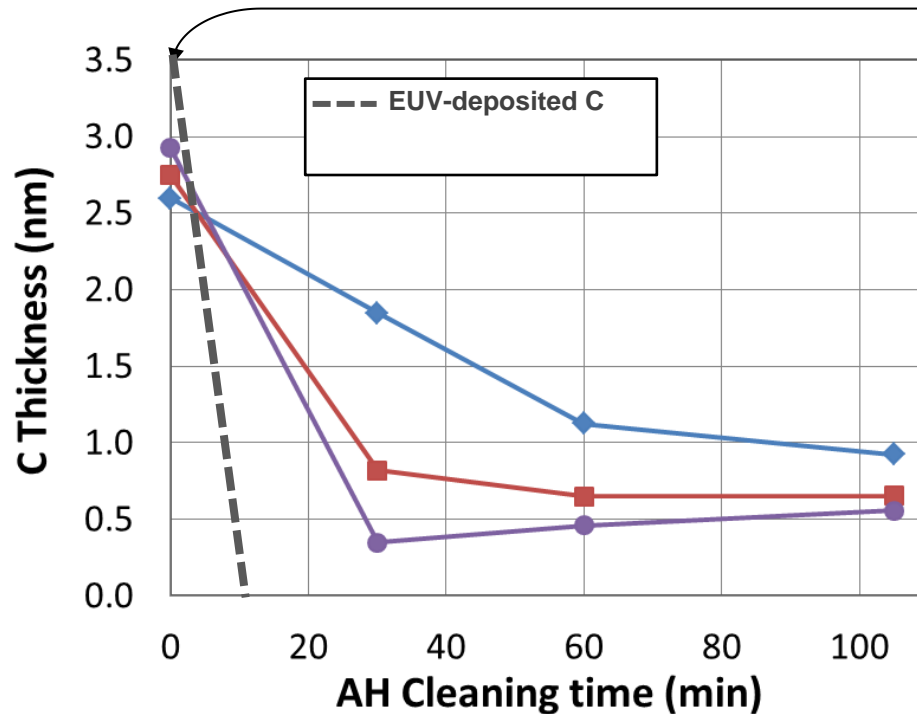
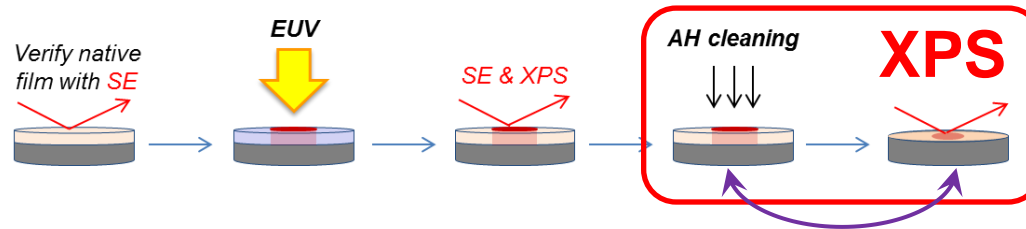


- Dose response from correlation of XPS maps and dose distributions across exposure spots
- Similar trends in EUV and e-beam data suggest two-step desorption process
- Electrons appear to desorb F $\sim 100\times$ more efficiently than EUV
- Does this mean that e-beam-based outgas tests are inherently insensitive to F contamination?

EUV interaction with PVDF

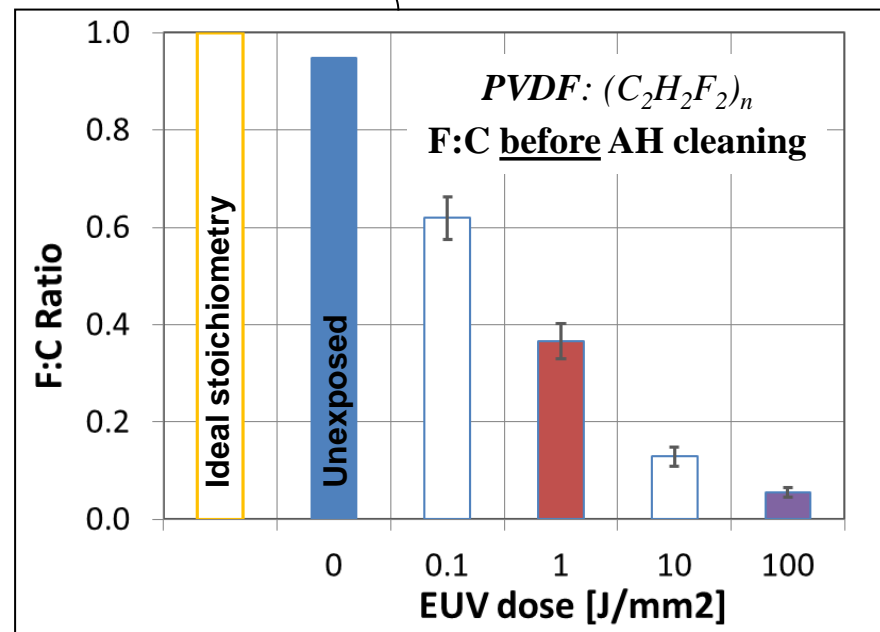
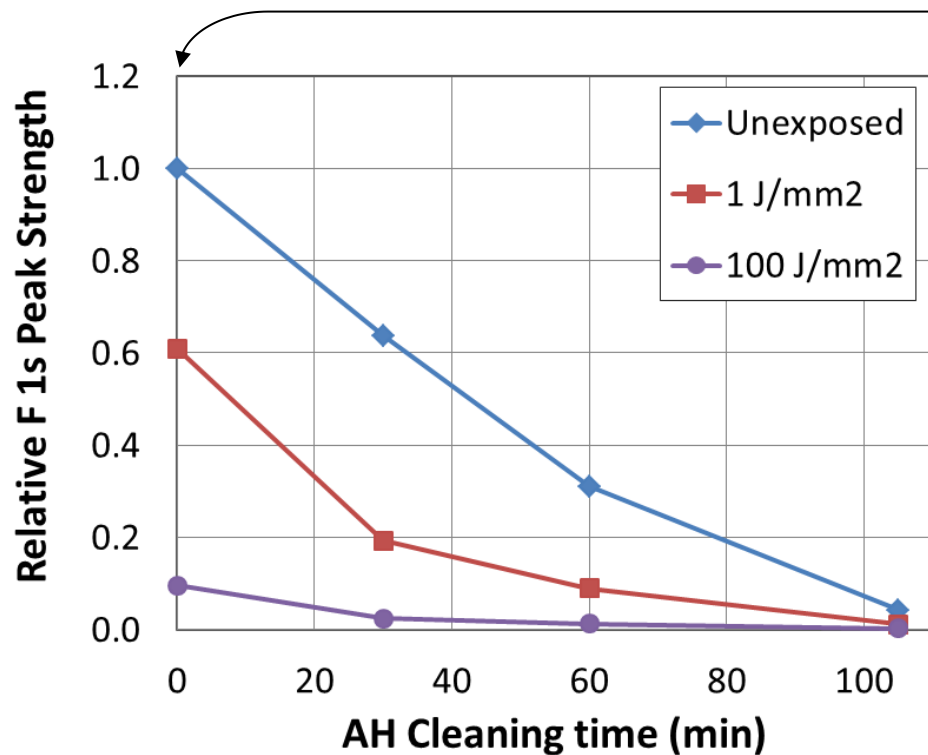
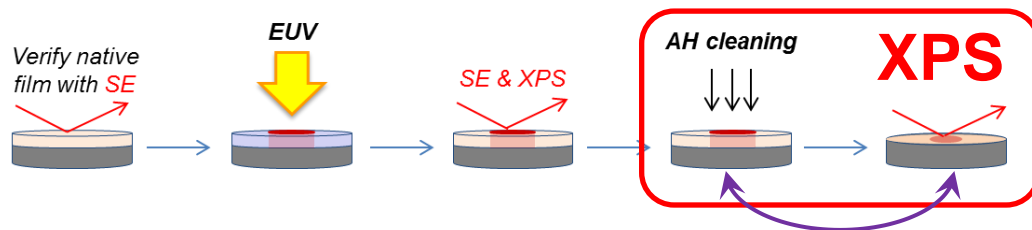


Atomic-H cleaning of PVDF: C removal



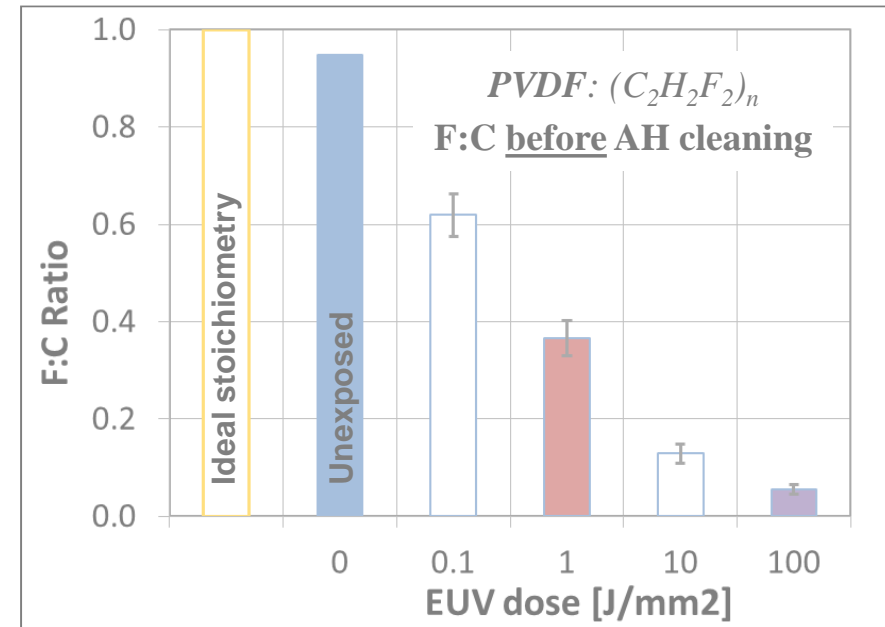
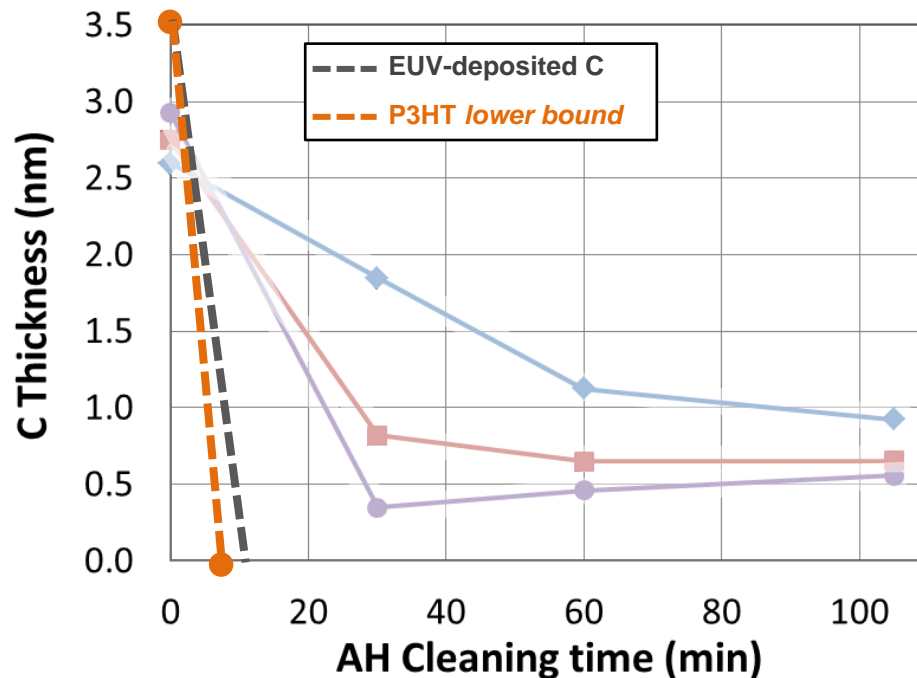
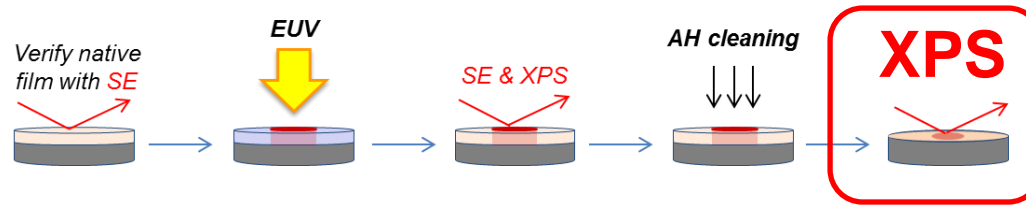
- The presence of F significantly slows overall cleaning rate of PVDF
- Areas exposed to high EUV doses have lower F:C ratios and hence clean fastest

Atomic-H cleaning of PVDF: F removal



- F is removed by AH at **very** slow rate
- The amount of F detected in XPS portion of outgas test could be artificially lowered by
 - Excessively long AH cleaning times (cleaning until all C is gone)
 - Witness sample intensity much higher than that expected on lowest-intensity NXE optic

AH cleaning of P3HT (S-containing polymer)

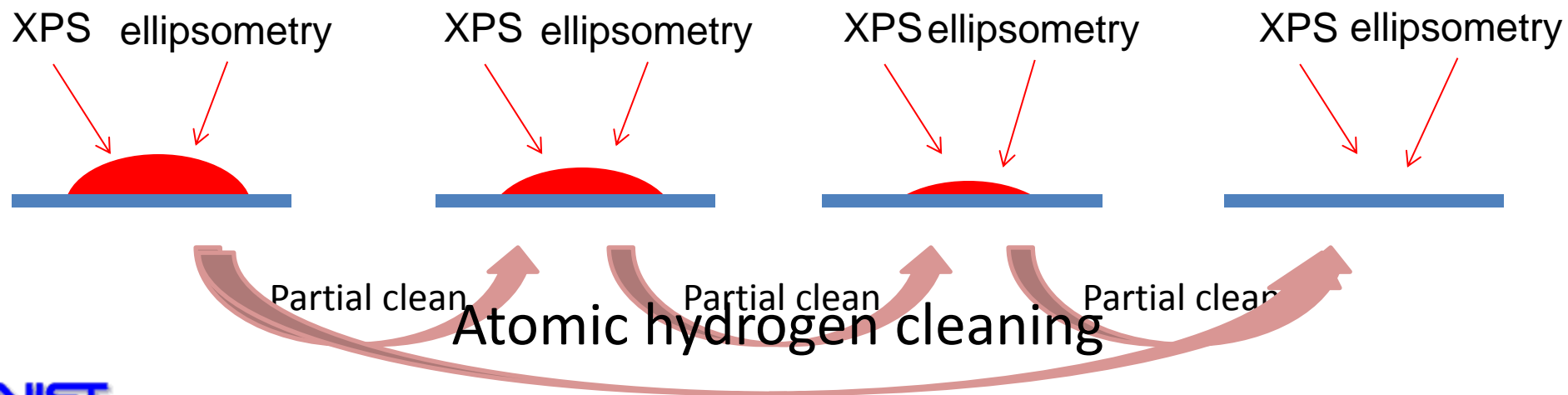


- AH removed all P3HT after first short cleaning interval
- AH cleaning rate for P3HT (S:C~10%) is at least as fast as typical EUV-deposited C.
- S is removed at least as quickly as C and does not affect C cleaning rate



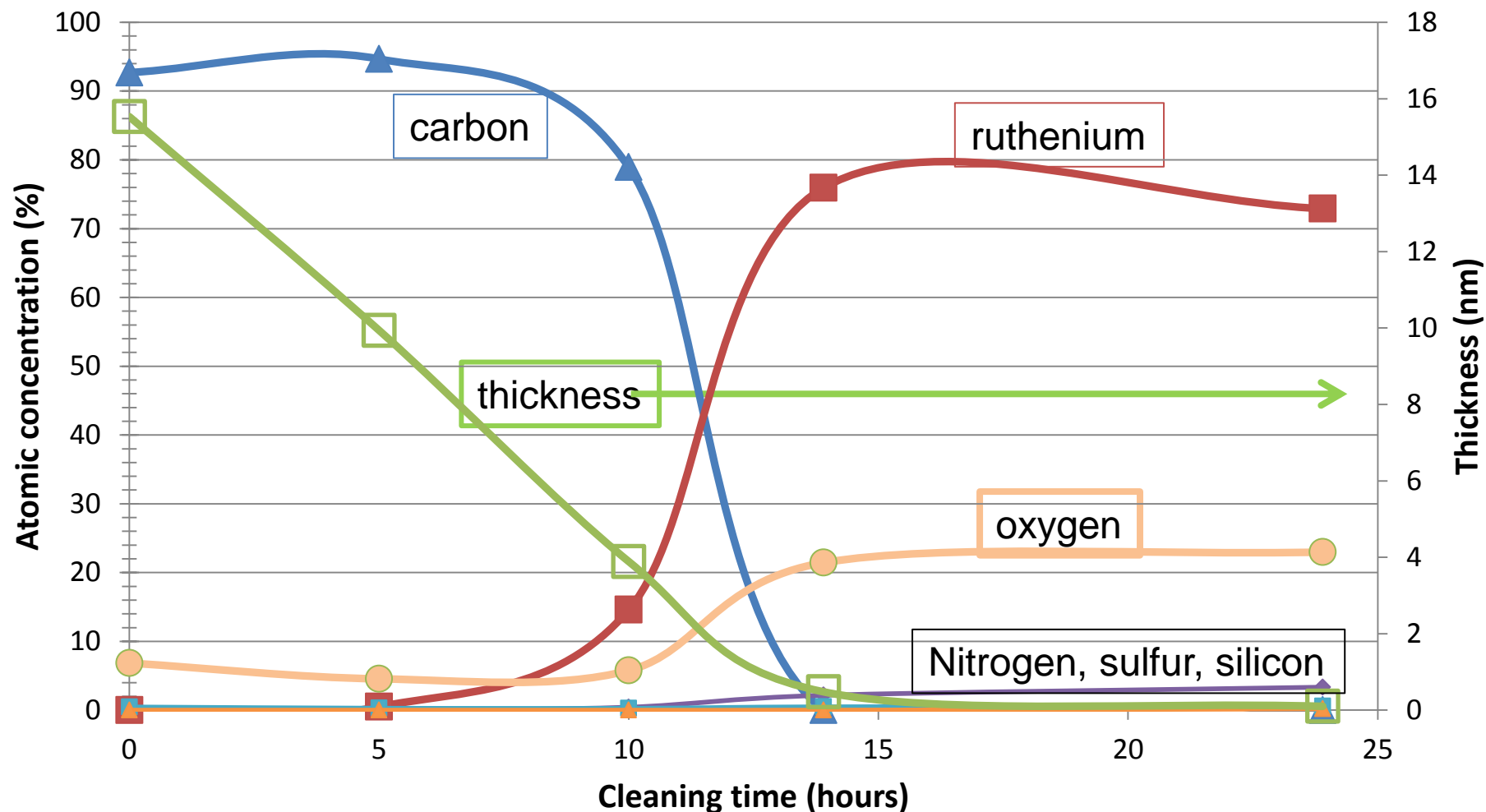
Studying the effectiveness of cleaning

- After over 100 customer samples, none have failed the non-cleanables specification
- We did more in depth measurements of one sample – it started with 15 nm of contamination growth
 - Measured XPS of the contamination spot PRIOR to cleaning
 - Partially cleaned multiple times with XPS after each clean cycle to measure the composition within the contamination, during cleaning, and after cleaning





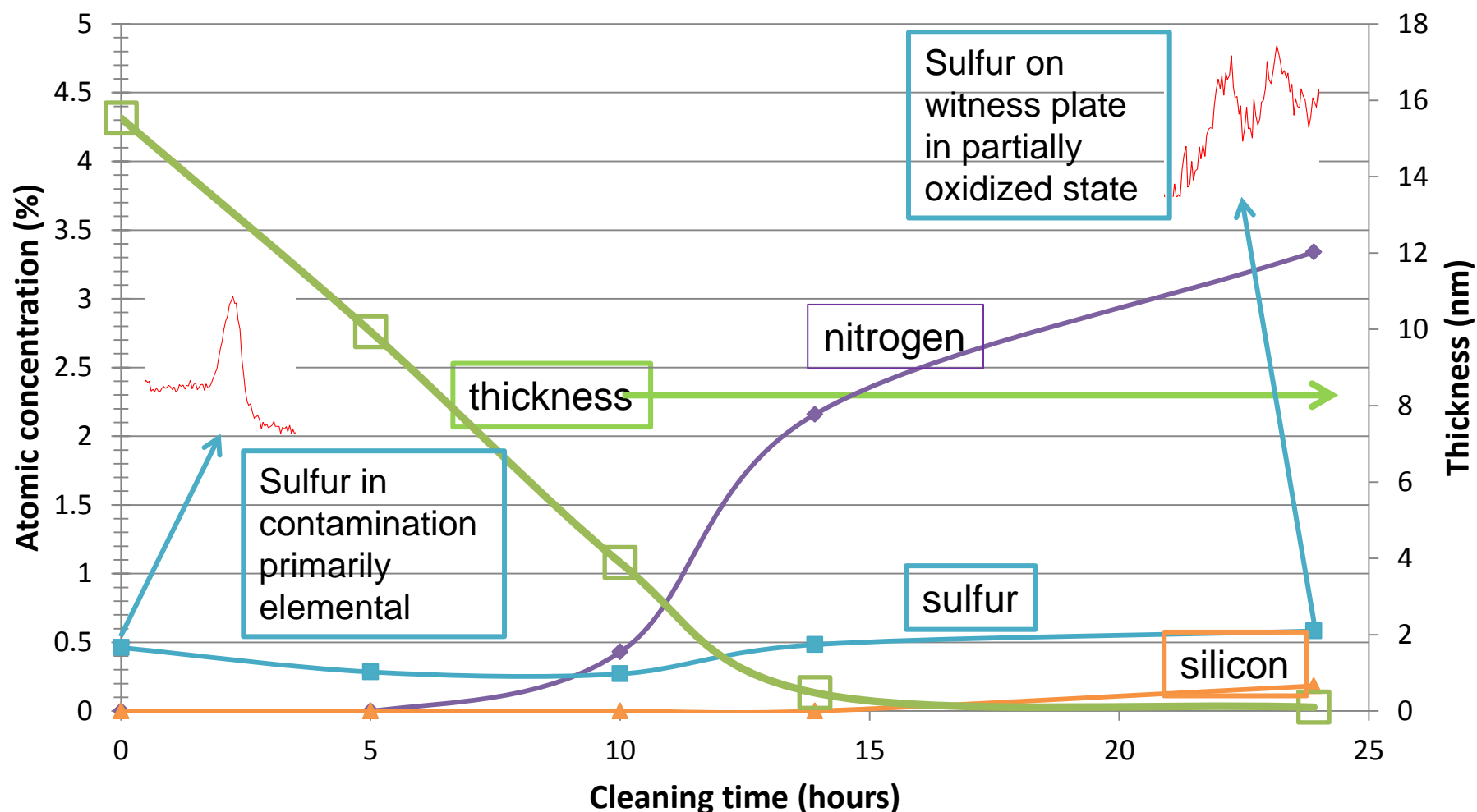
Composition between cleaning steps



- Primarily carbon contamination spot, after cleaning primarily ruthenium substrate
- Oxygen is present in the contamination, but at a higher level on the ruthenium substrate



Composition between cleaning steps



- Sulfur is present in both the contamination spot and the final cleaned ruthenium surface
- Sulfur in contamination is elemental, in/on ruthenium surface is sulfur oxide

Summary

- S-containing polymers and outgas contamination appear to clean at rate similar to pure EUV-deposited C.
- Atomic-H cleaning rate of C is significantly slowed by presence of F.
- F is rarely observed in outgas testing because it is efficiently desorbed by EUV & electrons *not* because it is efficiently cleaned by atomic H.
- Electrons desorb F (from polymer PVDF) ~100x more efficiently than EUV
 - Is e-beam outgas testing inherently insensitive to F contamination?
 - NIST and EIDEC systems use EUV on witness sample and have reported small amounts of F (< 1 atomic %) before AH cleaning.
 - Has F ever been seen in any e-beam test?